Synthesis and dielectric properties of $MgTiO_3$ and $Cu_{0.5}Ti_{0.5}NbO_4$ composite ceramics

A THESIS FOR THE PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF BACHELOR OF TECHNOLOGY

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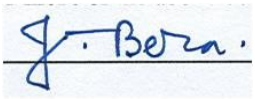
CERTIFICATE

This is to certify that the thesis entitled, **"Synthesis and dielectric properties of $MgTiO_3$ and $Cu_{0.5}Ti_{0.5}NbO_4$ composite ceramics"** submitted by Mr. Chinmay Sekhar Rout (Roll No 111CR0532) for the partial fulfilment for the requirements for the award of Bachelor of Technology degree in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in this thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.



Date: 26.06.2015

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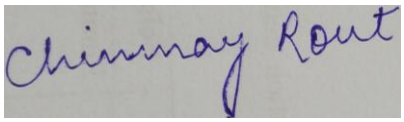

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Abstract

$MgTiO_3$ and $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics were synthesis through solid state reaction route. The phase formation behaviour during synthesis and after sintering was investigated using x-ray diffraction. The lattice parameter of $MgTiO_3$ was evaluated through Rietveld refinement of its XRD pattern. Composites of the two ceramics were prepared by mixing two pure phases and then sintering of compacts. The densification behaviour of composite ceramics was evaluated by measuring bulk density of sintered ceramics. Microstructure developed on sintered pellet was investigated using FESEM. Elemental mapping on sintered ceramics was performed using EDS. The dielectric permittivity, dielectric loss and impedance of the composite ceramics were measured using LCR meter. The properties of composite ceramics were co-related and explained.

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Introduction

Microwave dielectrics ceramics have attracted a considerable interest now a day because of their potential applications in mobile and satellite communication devices; as duplexer, resonator, antenna and oscillators, etc. Fig. 1 shows the resonators. The dielectric materials should have a moderate dielectric constant, low dielectric loss and near zero temperature coefficient of resonant frequency [1-4].

Fig. 1 MCV Dielectric resonators

Present generations wireless communication devices are becoming small in volume day by day. To meet this demand a high performance device with miniature microwave dielectrics material is urgently required. For the fabrication of a miniature device, low co-fired ceramics (LTCC) technology has received a considerable attention. For the fabrication of LTCC devices having microwave dielectrics materials, the dielectrics have to be sintered below $960^{o}C$ for co-firing of ceramics with silver electrode. The best commercialized microwave dielectric ceramics are $MgTiO_3$ and $BaMg_{1/3}Ti_{2/3}O_3$. However they are usually sintered at a temperature higher than $1200^{o}C$. The most common method to reduce the sintering

temperature of dielectric ceramics is the use of low melting glass or oxides as sintering additives. However these additives produce liquid during sintering which solidifies into a large amount of amorphous phase and remains in the grain boundary of ceramics. These amorphous glassy phases seriously degrade the microwave properties of dielectrics. Therefore research is going on to synthesis a new microwave dielectric compound which has the ability to be sintered below 960^{o}C without using any sintering additives.

$Cu_{0.5}Ti_{0.5}NbO_4$ ceramics is a new dielectric ceramics which has been reported to be sintered at a temperature of 960^{o}C and the material showed a very high quality factor of 11000 GHz [5]. The similar microwave dielectric ceramics $NiTiNbO_4$ also have been reported with a quality factor of 13500 GHz. However, that can only be sintered at 1125^{o}C [6].

As mentioned above the $MgTiO_3$ is the most commercialized microwave dielectric ceramics. However the material could be sintered at 1400^{o}C. But it has the highest quality factor among all mentioned above. The quality factor is ten orders higher than others i.e. in the range of 250000 GHz.

Hence, the mixture of two different types of microwave dielectric ceramics in a single body where one ceramics has low sintering temperature than other having high quality factor, may be an effective approach for making a composite microwave dielectric ceramics with reasonable low temperature sintering and quality factor characteristics.

Literature Review

$Cu_{0.5}Ti_{0.5}NbO_4$ ceramics has been reported to have the dielectrics constant of 71 and a quality factor of 11000GHz [Ching-Fang Tseng, Journal of the European Ceramic Society 35 (2015) 383–387]. Dependence of quality factor ($Q \times f$) value and temperature coefficient of the resonant frequencies (TCF) on the sintering temperature of $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics are shown in Fig. 2.

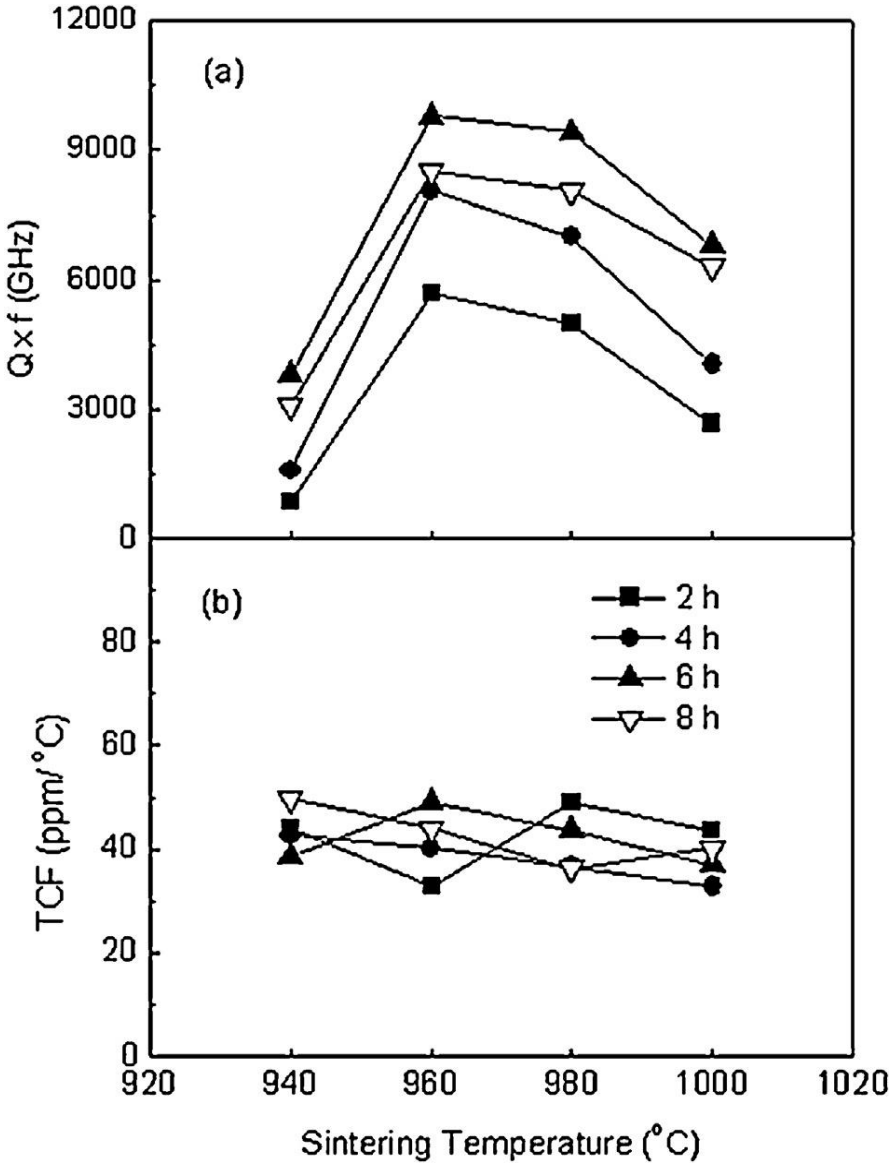

Fig. 2 Dependence of quality factor ($Q \times f$) value and TCF on the sintering temperature of $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics. (Taken from: Ching-Fang Tseng, Journal of the European Ceramic Society, 35 (2015) 383–387)

Similarly $Ni_{0.5}Ti_{0.5}NbO_4$ and $Co_{0.5}Ti_{0.5}NbO_4$ were also been reported to show dielectrics constant in the range of 60-64 and a quality factor in the range of 60000GHz-70000GHz. The quality factor of Ni0.5Ti0.5NbO4 ceramics with different ZnO additions are shown in Fig. 3 [Ching-Fang Tseng, Chao-Chen Chen, Chen-Wei Lin, Materials Chemistry and Physics, 147 (2014) 535-539].

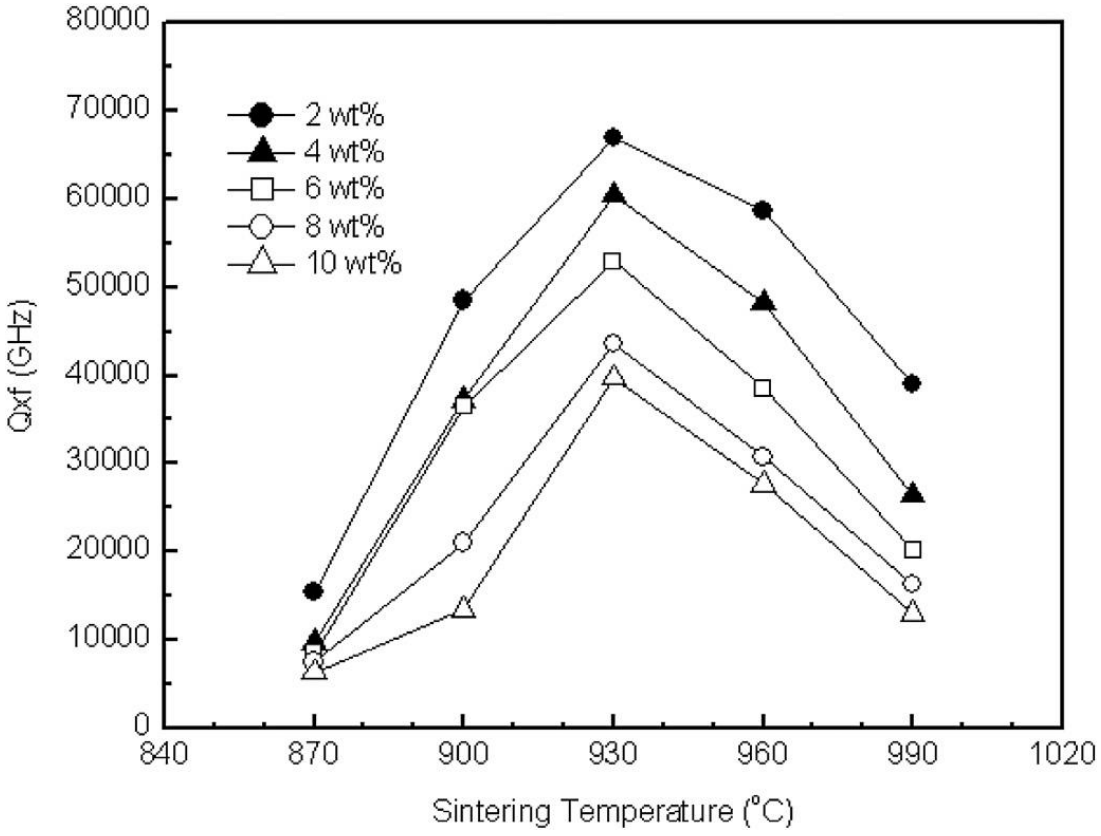

Fig. 3 The quality factor of Ni0.5Ti0.5NbO4 ceramics with different ZnO additions sintered at 870-990 ^{o}C for 6 h. (Taken from; Ching-Fang Tseng, Chao-Chen Chen, Chen-Wei Lin, Materials Chemistry and Physics 147 (2014) 535-539)

But these two ceramics i.e. $Ni_{0.5}Ti_{0.5}NbO_4$ and $Co_{0.5}Ti_{0.5}NbO_4$ requires a high sintering temperature of around 1100^{o}C and this is the disadvantage of these materials. So these materials are not suitable for LTCC microwave devices. The most important method used to reduce the sintering temperature is the addition of low melting glasses as sintering additives.

For example $MgTiO_3$-$CaTiO_3$ was sintered using ZnO, B_2O_3, SiO_2 based glass at a temperature of 875^oC and the ceramics show the dielectric constant of 10 and a quality factor of 7000.

It has been found in many other ceramic that when Cu is substituted for nickel or zinc, the sintering temperature of ceramics decreases. For that reason $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics have a low sintering temperature.

Objectives of Present Work

- The objective of present investigation is to synthesize a composite dielectric material containing the high quality factor $MgTiO_3$ and low temperature sinterable $Cu_{0.5}Ti_{0.5}NbO_4$.
- Synthesis of pure $MgTiO_3$ and pure $Cu_{0.5}Ti_{0.5}NbO_4$.
- Mixing of $Cu_{0.5}Ti_{0.5}NbO_4$ (CTN):$MgTiO_3$ (MT) in the ratio of 25:75, 50:50, 75:25 and to study the sintering behaviour, dielectrics properties of the composites.

Experimental

Powder Synthesis

Dielectrics compounds synthesized in the present investigation are shown in the Table 1. All these ceramics were synthesized through solid oxide route. The solid oxide reaction route uses simple processing steps and relatively less costly raw materials.

Table 1:- *List of compositions synthesized.*

1.	$Cu_{0.5}Ti_{0.5}NbO4$
2.	$MgTiO_3$
3.	50% $Cu_{0.5}Ti_{0.5}NbO_4$-50% $MgTiO_3$
4.	25% $Cu_{0.5}Ti_{0.5}NbO_4$-75% $MgTiO_3$
5.	75% $Cu_{0.5}Ti_{0.5}NbO_4$-25% $MgTiO_3$

Synthesis of $Cu_{0.5}Ti_{0.5}NbO_4$ (CTN)

The CTN powder was synthesized using Niobium Oxide (Nb_2O_5) (Merck India Ltd., Assay >99%), Titanium Oxide ($TiO_{2)}$ (Merck India Ltd., Assay >99%), Copper Oxide (CuO) (Loba Chemie)) as raw materials.

For a typical 10 gm batch composition, 1.86gm of CuO, 6.22gm of Nb_2O_5 and 1.86 gm of TiO_2 were mixed.The required amount of individual oxide powders were taken in an agate mortar and were mixed for 30 minutes. Iso-propanol liquid was used during mixing to have a better mixing of each component and to have homogeneity of the mixture. The above prepared CTN powder was calcined at 900^o C for 4hrs. The powder was re-calcined at 950^oC for 4hrs. The pure phase of the CTN was found after calcination of the precursor powder at

950^{o}C for 4hrs. The pellets were made using a pressing machine with a load of 4 Ton and a dwelling time of 90 seconds**.** The pellets were sintered at 1000^{o}C for 4 hrs.

Synthesis of $MgTiO_3$ (MT)

The MT powder was synthesized using Magnesium Oxide (MgO) (Merck India Ltd., Assay >99%), Titanium Oxide (TiO2) (Merck India Ltd., Assay >99%) as raw materials, using 3.68 gm of MgO and 6.64 gm of TiO_2. The powders were mixed for 30 minutes. The above prepared CTN powder was calcined at 950^{o}C for 4hrs. The powder was re-calcined at 1150^{o}C for 4hrs. The pure phase of the MT was found after calcination of the precursor powder at 1150^{o}C. The pellets were made and were sintered at 1300^{o}C for 4 hrs.

Synthesis of 50%$Cu_{0.5}Ti_{0.5}NbO_4$ (CTN) - 50%$MgTiO_3$ (MT)

The 50 vol % $Cu_{0.5}Ti_{0.5}NbO_4$ (CTN) – 50 vol % $MgTiO_3$ (MT) composite was prepared by using 1.665gm of pure phase CTN powder and 1.335 gm of pure phase MT powder. The powders were mixed for 30 minutes. Composite pellets were made at a load of 4 Ton and a dwelling time of 90 seconds**.** Pressed pellets were sintered at 1125^{o}C for 4 hrs.

Synthesis of 25% $Cu_{0.5}Ti_{0.5}NbO_4$ (CTN) - 75%$MgTiO_3$ (MT)

The 25 vol % $Cu_{0.5}Ti_{0.5}NbO_4$ (CTN)-75 vol % $MgTiO_3$ (MT) composite was prepared by mixing, 0.90gm of CTN powder and 2.10 gm of MT powder and then pressing pellets followed by sintering at 1190^{o}C for 4 hrs.

Synthesis of 75% $Cu_{0.5}Ti_{0.5}NbO_4$ (CTN) - 25%$MgTiO_3$ (MT)

The 75% $Cu_{0.5}Ti_{0.5}NbO_4$ (CTN) - 25% $MgTiO_3$ (MT) composite was prepared by using 2.37gm of CTN powder and 0.63gm of MT powder. Pellets were sintered at 1065^{o}C for 4 hrs.

Characterization of powder

Phase analysis

Phase formation behaviour was studied using powder X-ray diffraction (XRD) analysis (RIGAKU JAPAN/ULTIMA-IV instrument). The source radiation used is Cu K_α with a wavelength of 1.541874 Å and equipped with Ni β-filter. Bragg-Brentano focusing principle is used for the measurement of the intensity of diffraction. The current and voltage used during the experiment are of 40 kV and 40 mA, with a step size of 0.05^o. The identification of different phases was carried out by Hanawalt method using X-pert Highscore software.

Fabrication of pellet and Sintering

The pure phase powders were mixed with 3 weight % polyvinyl alcohol (PVA) as granulating additive. The granulated powder was pressed into circular disks using stearic acid as a lubricant. Pellets were compacted at a pressure of 4 ton with a holding time of 90 seconds and were sintered at different temperatures depending on the compositions. Sintering temperature/time for different composition is shown in Table 2.

Table 2:-. *Sintering temperature/time for different compositions.*

	Composition	**Sintering temperatures**
1.	$Cu_{0.5}Ti_{0.5}NbO_4$	1000^oC/4hrs.
2.	$MgTiO_3$	1300^oC/4hrs.
3.	50% $Cu_{0.5}Ti_{0.5}NbO_4$-50% $MgTiO_3$	1125^oC/2hrs
4.	25% $Cu_{0.5}Ti_{0.5}NbO_4$-75% $MgTiO_3$	1190^oC/2hrs
5.	75% $Cu_{0.5}Ti_{0.5}NbO_4$-25% $MgTiO_3$	1065^oC/2hrs

Density measurements

The density of the sintered samples was measured by Archimedes principle. The sintered samples were immersed in water and kept under vacuum till the water filled up the open pores completely. The suspended weight of the pellet was measured by hanging the pellet on the hanger inside the water. The soaked weight was then measured by removing excess water from the pellet with a wet paper. The bulk density was calculated from the formula:

$$D_{bulk} = \frac{W_{dry}}{W_{soak} - W_{sus}}$$

Where, W_{dry} = Dry weight of the sample, W_{soak} = Soaked weight of the sample,

W_{sus} = Suspended weight of the sample.

Theoretical density was calculated from unit cell volume determined by X-ray method using the formula:

$$\rho = \frac{\Sigma A_w}{NV}$$

where, ρ is the theoretical (X-Ray) density (gm/cc), ΣA_w is the sum of the atomic weights of all the atoms in the unit cell, N is the Avogadro's number and V is the volume of unit cell (cc).

The apparent porosity of the sintered samples was calculated from the formula:

$$\text{Apparent Porosity} = \frac{(W_{soak} - W_{dry})}{(W_{soak} - W_{sus})}$$

Where, W_{dry} = Dry weight of the sample, W_{soak} = Soaked weight of the sample,

W_{sus} = Suspended weight of the sample.

Microstructural study

The surface morphology of the sintered specimen was studied using field emission scanning electron microscope (FE-SEM) NANO-NOVA, FEI. In FESEM, a field emission cathode in electron gun under vacuum emits electron beam which passes through a series of electromagnetic lenses. The sample is bombarded with the fine beam of electrons having acceleration potentials ranging from 0.5 to 30 kV. Images were taken in low vacuum secondary electron beam. The as-sintered samples were used for studying microstructure.

Dielectric Measurements

For electrical measurements, both surfaces of a pellet were painted with silver conductive paste (Alfa Aesar) and cured at 650^{o}C for 30min. Thus, a pellet with two parallel electrodes acts as a single layer capacitor. The capacitance (*C*), dielectric constant (ε') and dielectric loss (*tan* δ) of this disc capacitor was measured using HIOKI LCR meter in the frequency range 40Hz – 1MHz.

The capacitance (*C*) of a capacitor is given by;

$$C = \frac{\varepsilon\, \varepsilon_o A}{d}$$

Where, ε_o is the permittivity of free space (8.854 x 10^{-12} F/m), *A* is the area of the electrodes and *d* is the thickness of the dielectrics. ε is the relative permittivity which is dimensionless, ε can be explained by:

$$\varepsilon = \varepsilon' + i\varepsilon''$$

$\mathcal{E}'$ and $\mathcal{E}''$ are the real and imaginary part of relative permittivity.

The dielectric loss (*tan* δ) is the measure of energy dissipated in a dielectric on application of an electric field, which is expressed as:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

Impedance Spectroscopy

Impedance spectroscopy is a powerful tool for investigation of complex electrical properties. The technique is advantageous in separating and determining the values of grain and grain boundary effects, and also helpful in correlation with the properties such as composition, microstructure, defects, dielectric properties, etc.

Results and Discussion

Phase Analysis: $MgTiO_3$

The mixed powders were calcined first to form the phase. The phase transformation was investigated using XRD analysis. Fig. 4 shows the XRD pattern of $MgTiO_3$ powder prepared after calcination at 1150^{o}C and 1250^{o}C. The XRD pattern of powder calcined at 1150^{o}C (Fig. 4(a) shows major peaks for $MgTiO_3$ mainly. However, there were the presence of TiO_2 and MgO peaks as indicated in the figure. These peaks were absent in the 1250^{o}C calcined powder.

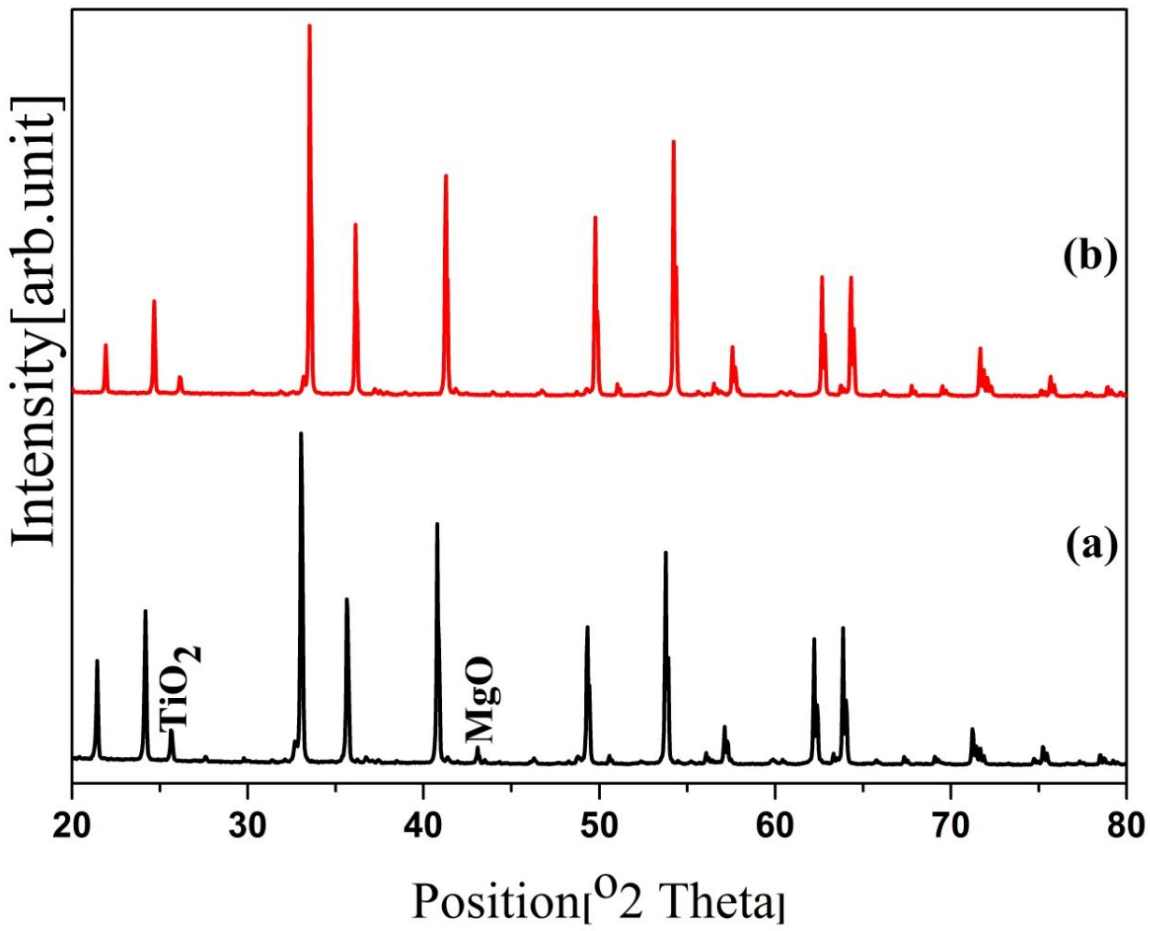

Fig. 4 *Room temperature XRD pattern of MgTiO3 (MT) precursor powder calcined at (a) 1150^{o}C, (b) 1250^{o}C. Major phases identified are also shown in the figure.*

So, the pure phase of $MgTiO_3$ was formed at 1250^oC calcination temperature. This powder was pressed and sintered at 1300^oC .The sintered pellets were also investigated through XRD analysis. **Fig 5** shows the Rietveld refinement output of the XRD pattern obtained on sintered $MgTiO_3$ pellets. Lattice parameters of MT were refined by Rietveld refinements using MAUD program, considering space group $R\bar{3}$ for the structure [Materials Chemistry and Physics 117 (2009) 192–198]. Initial cell parameters, atomic coordinates and atomic displacements parameters for the refinement were taken from the reference. The refinement consisted of the parameters set including the modeling of background scale factor, lattice parameters, detector zero point and profile parameters, etc. Final lattice parameters and *R*-factors after refinement are: a= 5.0468, c= 13.8793 Å and R_w=14.38 %, R_b=9.85 %, Sigma=3.35, respectively. Refined atomic coordinates of $MgTiO_3$ unit cell are shown in **Table 3**.

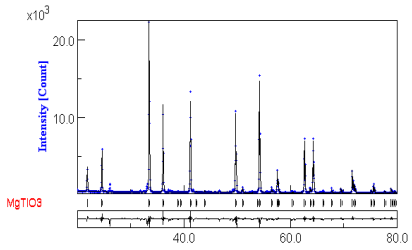

Fig. 5 *Rietveld refinement plot for sintered $MgTiO_3$ ceramics, showing observed (+), calculated (solid line) XRD profile, their differences in the bottom and position of allowed Bragg reflections (tick marks).*

***Table 3*:-** *Rietveld refinement results for atomic coordinates of $MgTiO_3$ unit cell.*

Element Name	X	y	Z	Occupancy
Mg	0.0004	0.0004	0.3581	1.06
Ti	0.0004	-0.0002	0.1449	0.98
O	0.3218	0.0141	0.2513	0.97

$Cu_{0.5}Ti_{0.5}NbO_4$ (CTN)

$Cu_{0.5}Ti_{0.5}NbO_4$ (CTN) ceramics composition were calcined at 900, 950, 1000^oC. **Fig 6** shows the XRD pattern of those calcined powder. The powder, which was calcined at 900^oC, shows the formation of CTN phase. The intermediate phase $CuNb_2O_6$ was also present (marked in the figure). The amount of intermediate phase $CuNb_2O_6$ was lower in 950^oC calcined powder as the peak height for the corresponding phase was lower.

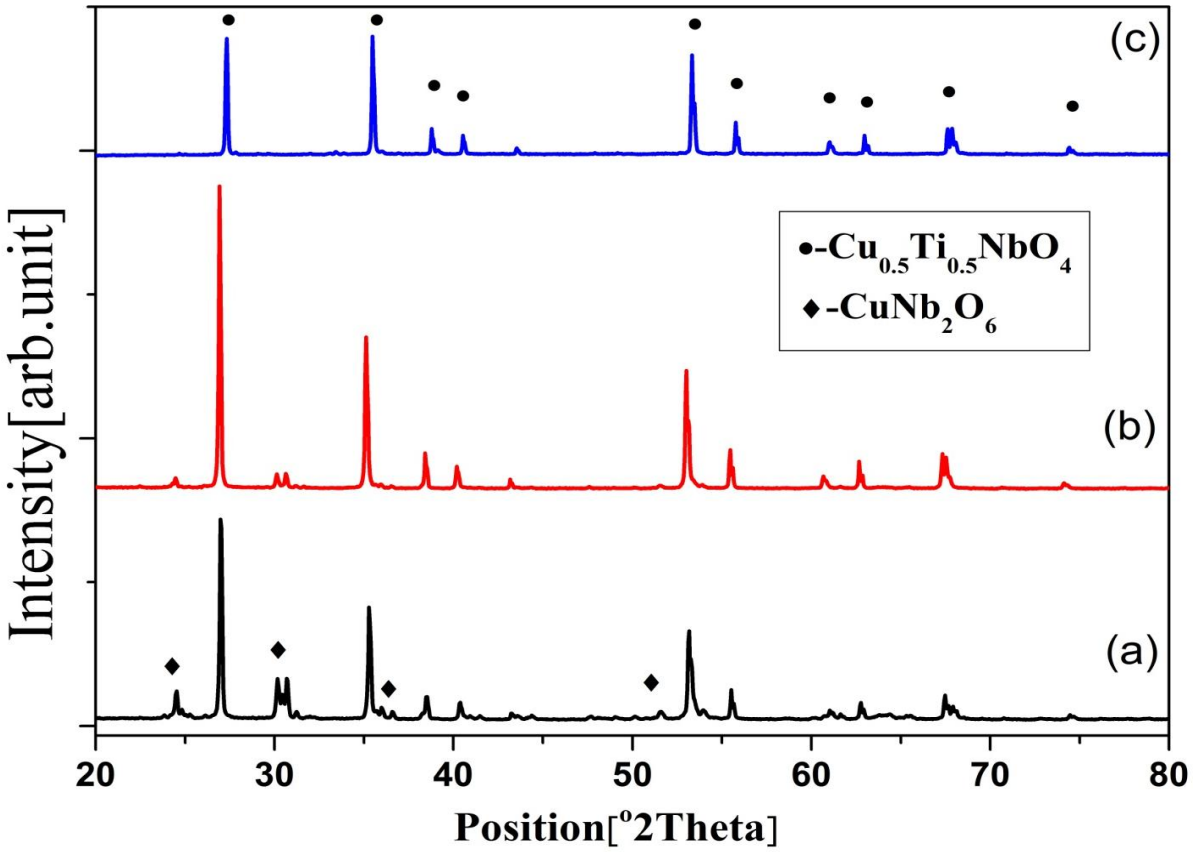

Fig. 6 Room *temperature XRD pattern of $Cu_{0.5}Ti_{0.5}NbO_4$ (CTN) precursor powder after calcined at (a) 900^oC, (b) 950^oC, (c) 1000^oC.*

Fig 6(c) shows the XRD pattern of the powder that calcined at 1000^{o}C. The pattern shows almost pure $Cu_{0.5}Ti_{0.5}NbO_4$ phase. Unfortunately, $Cu_{0.5}Ti_{0.5}NbO_4$ crystal data was not available to us and the Rietveld refinement for the compound could not be performed. However, the pattern was matched with the standard JCPDS file number 46-0524 for $Cu_{0.5}Ti_{0.5}NbO_4$ phase. **Fig 7** shows the peak list those compared with the standard file.

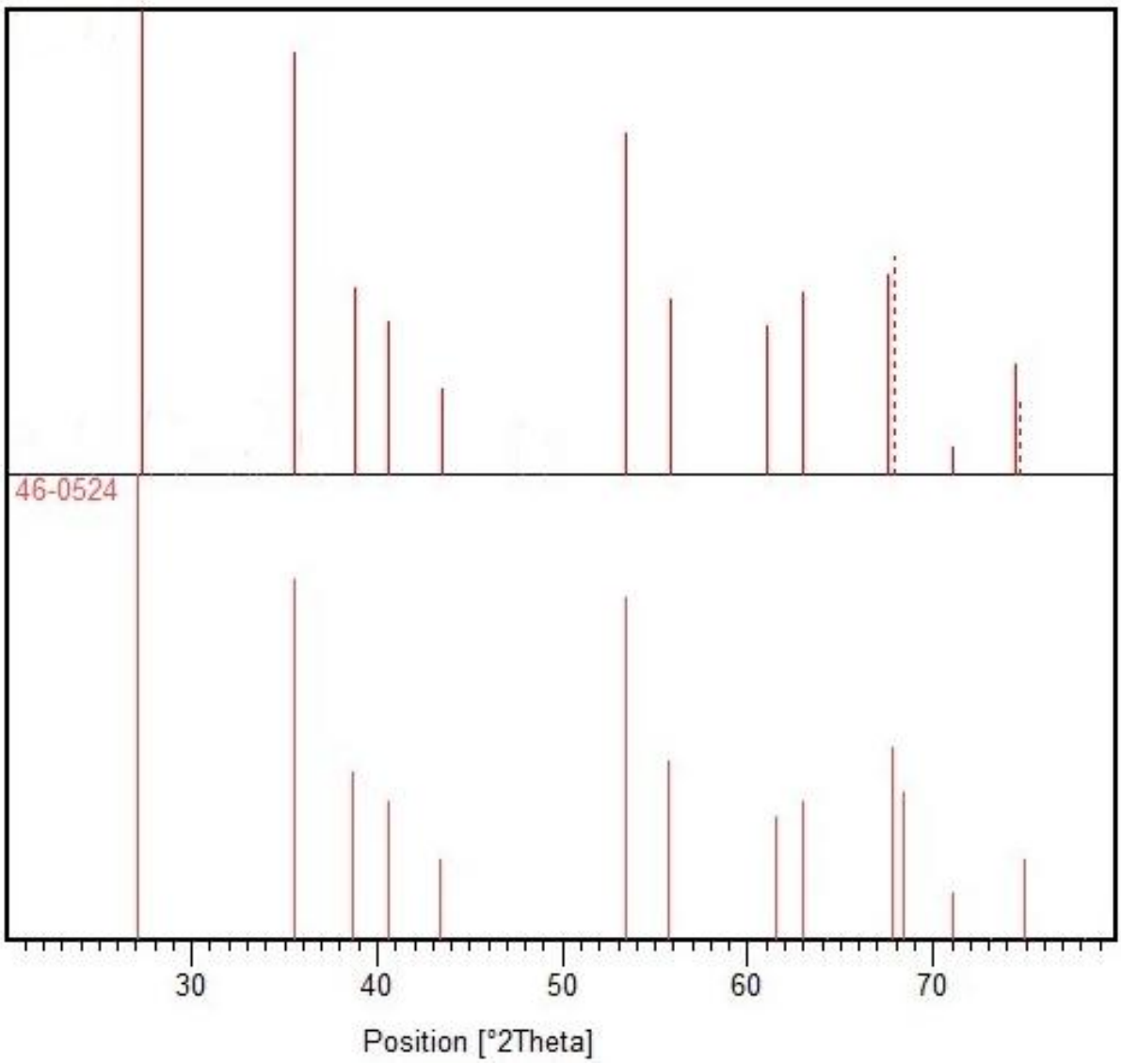

***Fig. 7** shows the peak list compared with the standard JCPDS file for $Cu_{0.5}Ti_{0.5}NbO_4$.*

$Cu0.5Ti_{0.5}NbO_4$ (CTN)-MgTiO3 (MT) Composite

The CTN-MT composite with three different ratios in volume % such as 25%CTN-75%MT,50%CTN-50%MT,75%CTN-25%MT were sintered at 1065^{o}C,1125^{o}C,and 1190^{o}C respectively because MT requires the high temperature for sintering. **Fig 8** shows the XRD pattern of three composites along with the pure CTN and MT phases. The phase identifications were conducted in the three composites. The identifications showed that with increase in CTN phase in the composite the two phases i.e. CTN and MT reacts with each other to produce different intermediate phases. The reaction was lowest in 25%CTN-75%MT i.e. in the composite where CTN amount was lowest. The identification of phases was very difficult due to the formation of many unknown phases. However, there was a common observation that CTN reacts with MT to form $MgNbO_3$ (Magnesium Niobiate) compound releasing copper oxide phases in the system.

Bulk Density and Apparent Porosity

Fig. 9 shows variation of bulk densities for different composition BD values are shown in **Table 4**. The figure shows that $MgTiO_3$ has lowest bulk density and $Cu_{0.5}Ti_{0.5}NbO_4$ has highest bulk density. When 25% $Cu_{0.5}Ti_{0.5}NbO_4$ is added to $MgTiO_3$ the bulk density rapidly increased due to the formation of liquid phase and better densification by the addition of $Cu_{0.5}Ti_{0.5}NbO_4$. After that bulk density gradually increases with the increase in $Cu_{0.5}Ti_{0.5}NbO_4$. **Fig 10** shows the variation of apparent porosity for different composition. Apparent porosity was very high in $MgTiO_3$ ceramics this is due to the insufficient sintering of the ceramics .The ceramics are sintered at 1250^{o}C. The apparent porosity rapidly decreases to about only 5% from 30% by the addition of 25% of $Cu_{0.5}Ti_{0.5}NbO_4$ to $MgTiO_3$. After that apparent porosity was almost same in other samples. Rapid decrease in apparent porosity is due to the filling of pores by the liquid phase which formed when $Cu_{0.5}Ti_{0.5}NbO_4$ was added.

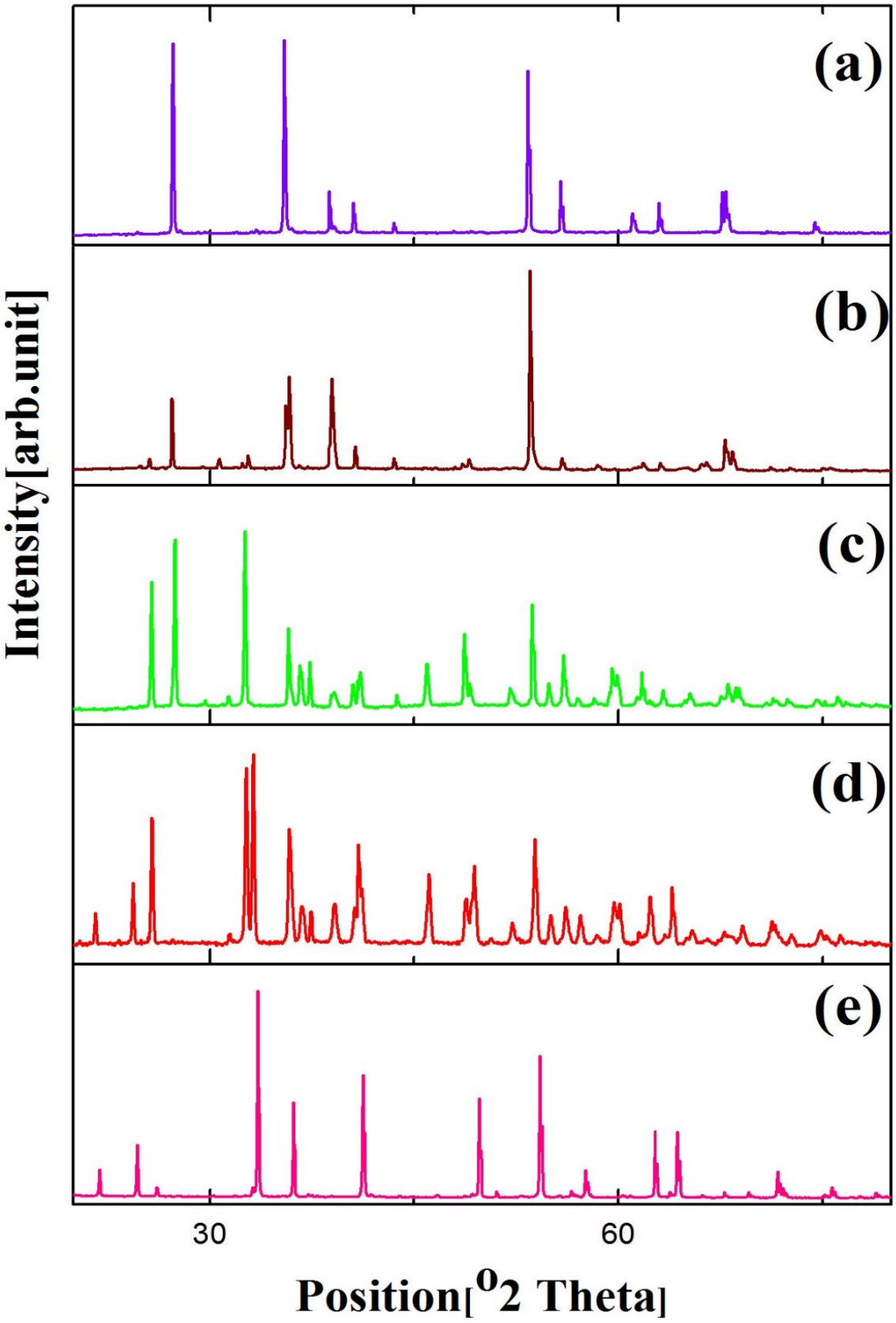

Fig 8 *XRD pattern of the (a) pure Cu0.5Ti0.5NbO4 (CTN), (b) 75CTN:25MT, (c) 50CTN:50MT, (d) 25CTN:75MT, (e) $MgTiO_3$ (MT) phases.*

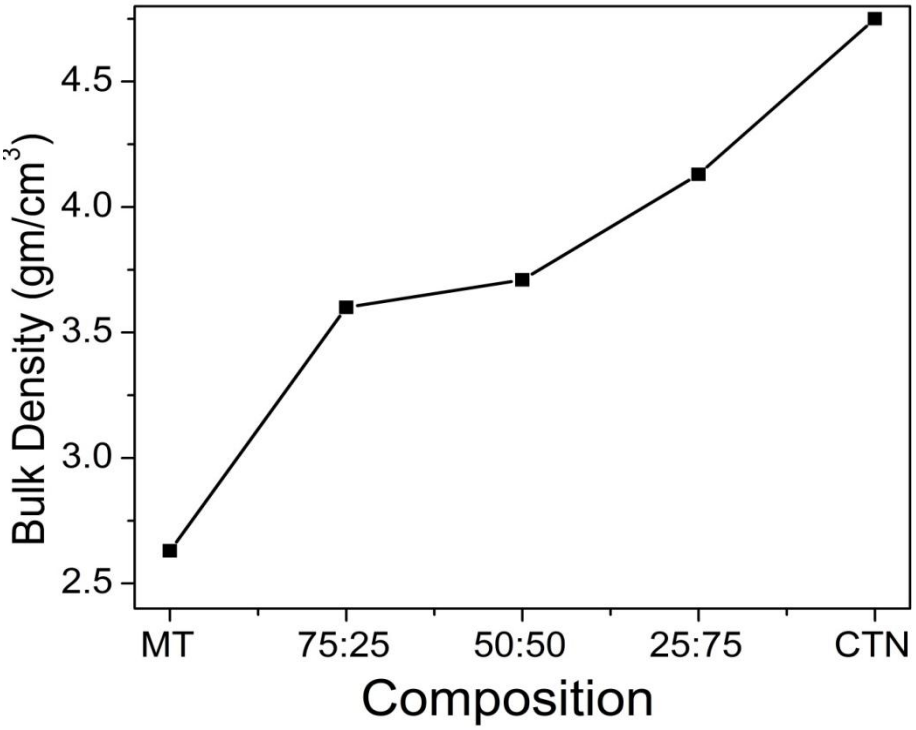

Fig 9 *Bulk Density of pure $MgTiO_3$(MT), pure $Cu_{0.5}Ti_{0.5}NbO_4$(CTN) and different composites.*

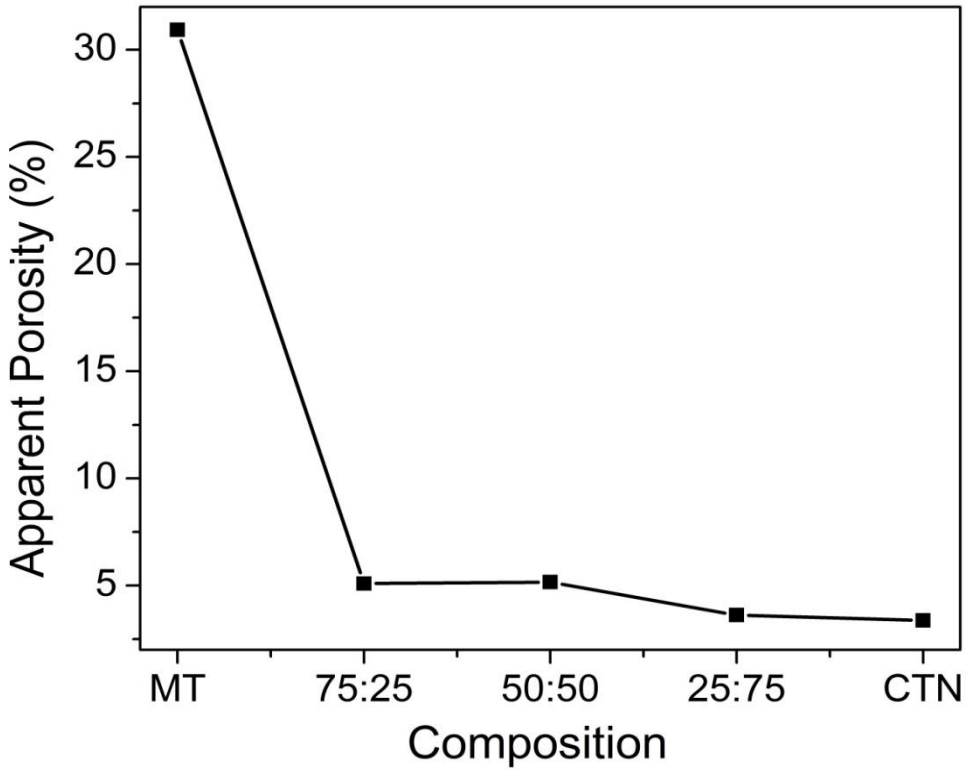

Fig 10 *Apparent Porosity of pure $MgTiO_3$(MT), pure $Cu_{0.5}Ti_{0.5}NbO_4$ (CTN) and different composites.*

MICROSTRUCTURAL ANALYSIS

Fig. 11(a) shows the surface microstructure of sintered $MgTiO_3$ ceramics. It shows that the grains are cubical and sizes are in the range of 3-10 micron. The broken surface microstructure of $MgTiO_3$; **Fig. 11(b)** contains both open and close porosity.

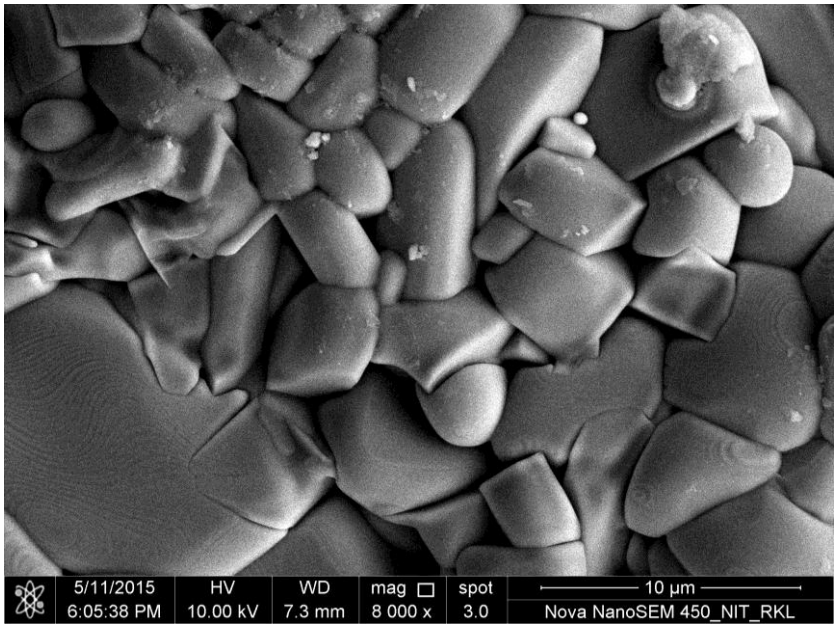

Fig. 11(a) *$MgTiO_3$ sintered pellet surface; grains are in the range 3 to 10 microns.*

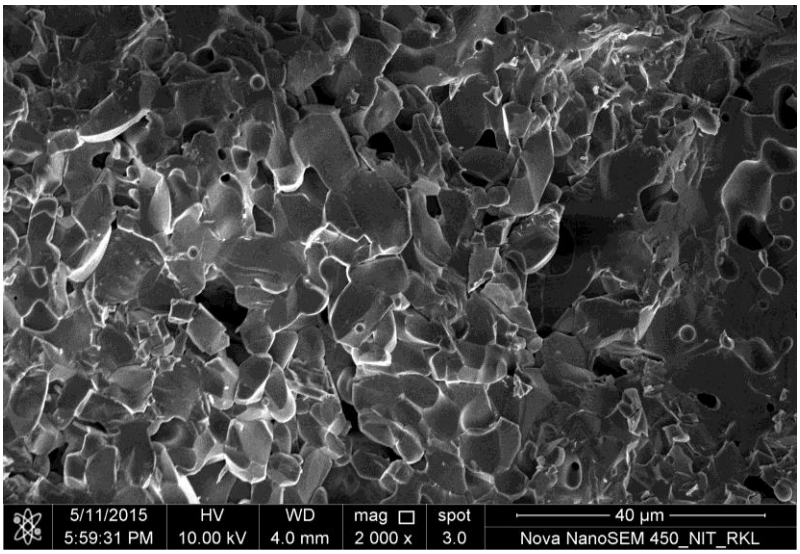

Fig. 11(b) Microstructure of $MgTiO_3$ broken surface having both open and close porosity.

Fig. 11(c) and (d) shows the microstructure of $Cu_{0.5}Ti_{0.5}NbO_4$ sintered pellet surfaces and bulk respectively. The surface microstructure shows duplex microstructure having some elongated grains surrounded by many small grains and pores inside the grains. However, the broken bulk surface shows a very compact structure. Although there were many closed porosity inside the grain and very few open porosity along grain boundaries. This indicates that the sintering was very fast in the ceramics due to the formation of liquid phase.

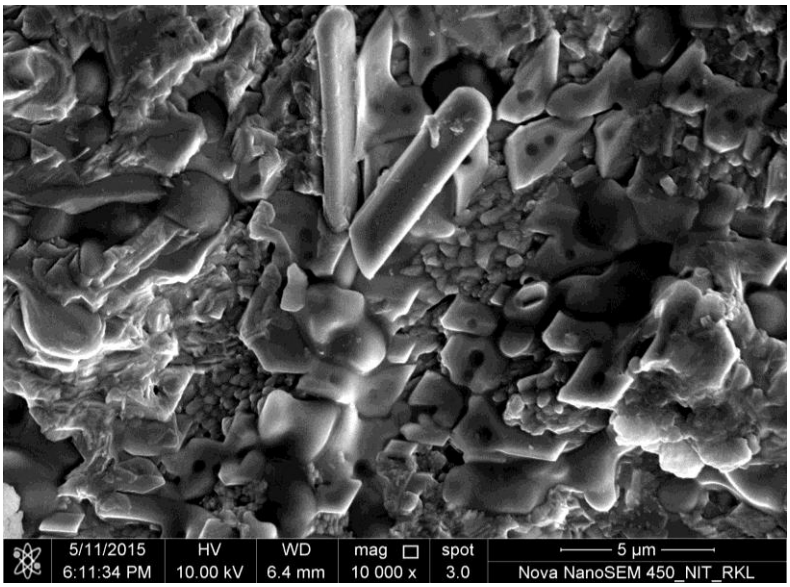

Fig. 11(c) *Cu0.5Ti0.5NbO4 ceramics sintered pellet surface.*

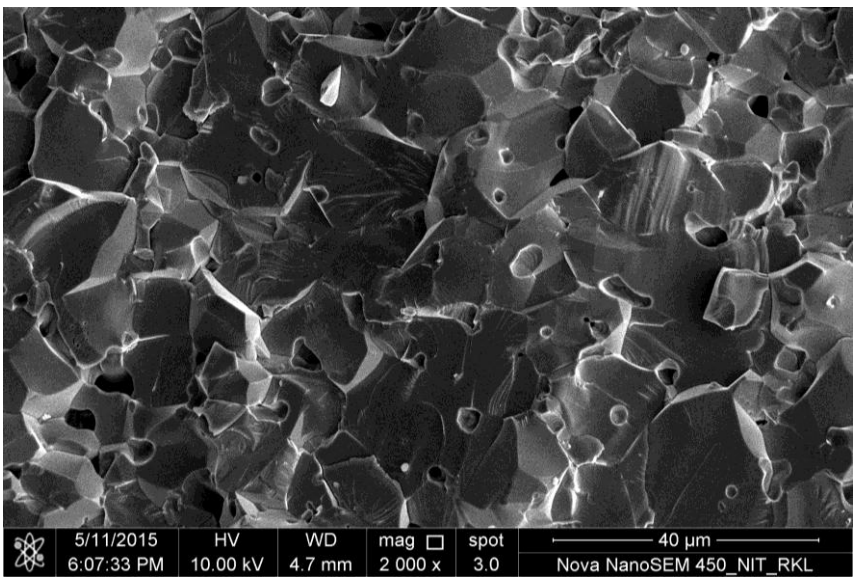

Fig. 11(d):- *Shows a porous structure of $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics.*

Fig. 11(e) shows the 50:50 (CTN): (MT) composites ceramics. Figure shows a typical liquid phase sintered microstructure. **Fig. 11(f)** shows elemental mapping with different colour code. Mapping shows that copper containing phases are segregated at the grain boundaries between mainly two different types of grains such as Mg based and Nb based. This indicates that $MgTiO_3$) reacts with $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics to produce a low melting liquid mainly containing copper oxide.

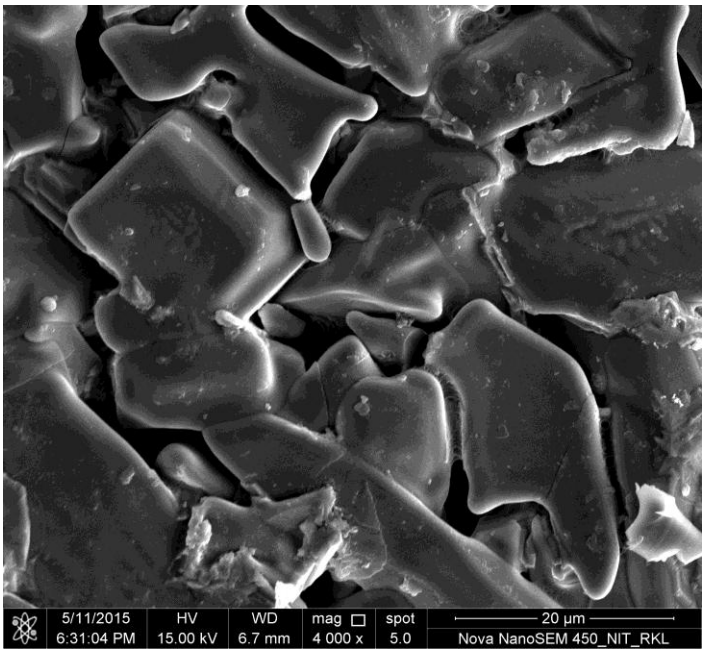

Fig. 11(e) ***T****ypical liquid phase sintered microstructure of 50:50* $MgTiO_3$ *(MT):* $Cu_{0.5}Ti_{0.5}NbO_4$ *(CTN) ceramics.*

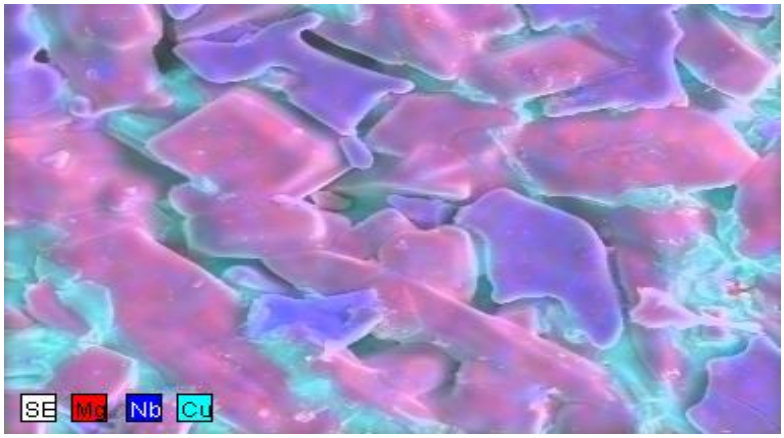

Fig. 11(f) *Elemental mapping of the 50:50* $Cu_{0.5}Ti_{0.5}NbO_4$ *(CTN):* $MgTiO_3$ *(MT) Surface.*

Dielectric Properties

Fig. 12 shows the frequencies dependence of permittivity. Permittivity graphs shows that $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics has highest and MT has lowest permittivity among all. The permittivity of $Cu_{0.5}Ti_{0.5}NbO_4$ rapidly decreases with the increase in frequency. Composites ceramics has the permittivity in between two pure end members. For example, $Cu_{0.5}Ti_{0.5}NbO_4$ (CTN):$MgTiO_3$ (MT) i.e. 75:25 composites has highest permittivity among three composites. In all cases permittivity decreases with the increase in frequency which is due to the relaxation of polarization at higher frequency. Dipole orientation does not follow the frequency change at higher frequency for that reason effective polarization decreases with the increase in frequency.

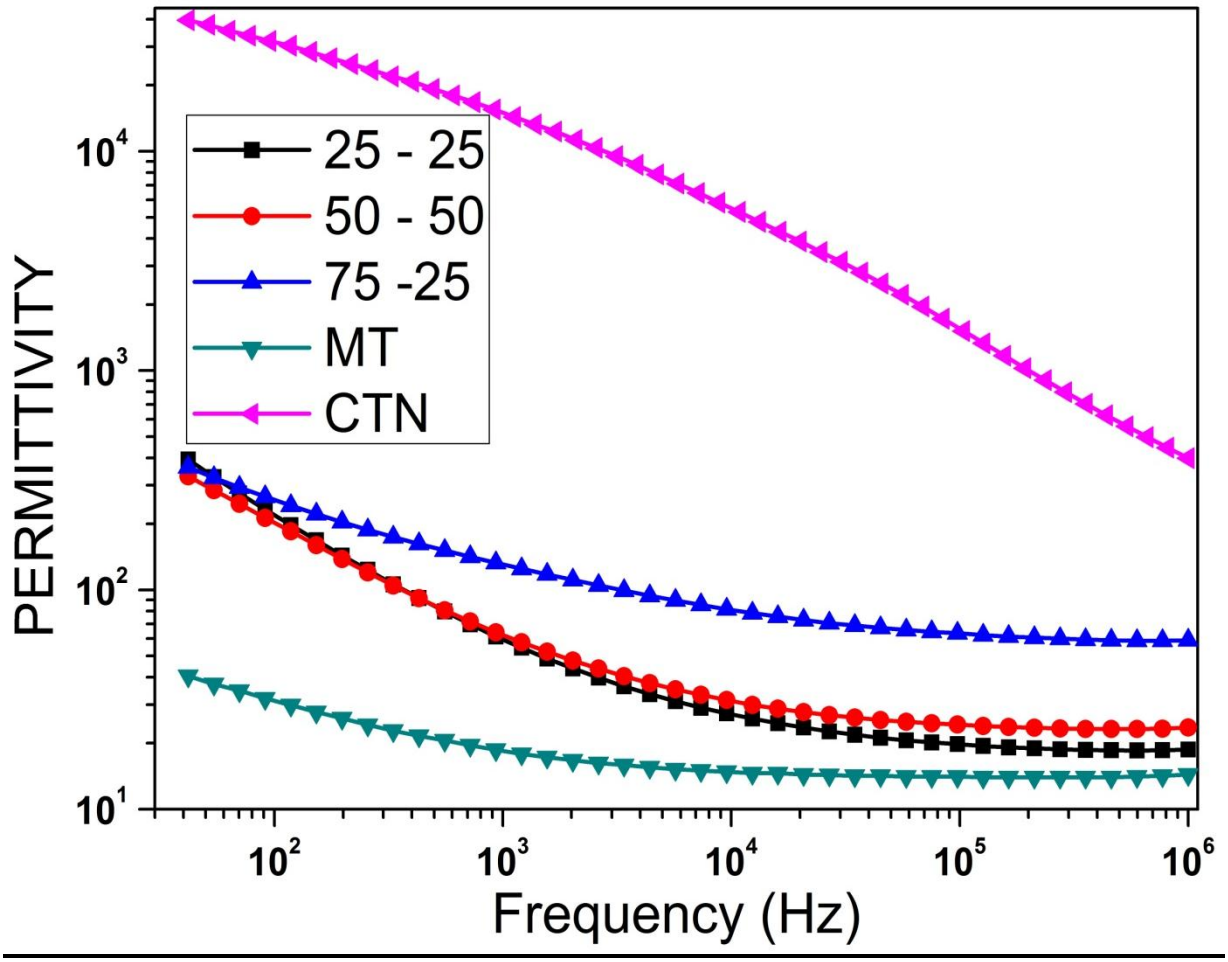

***Fig. 12 V**ariations of permittivity with frequency for different compositions.*

Fig. 13 shows the variation of dielectric loss with frequency. CTN ceramics has lower loses at lower frequency and that loss increases with the increase in frequency. However, for other ceramics like $MgTiO_3$ and composites, all have higher losses at lower frequency and lower loses at higher frequency. The result indicates that high loses of $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics at 1MHz can be effectively reduce by the addition of small amount of $MgTiO_3$ which is very useful for high frequency microwave application of $Cu_{0.5}Ti_{0.5}NbO_4$ based ceramics composites with $MgTiO_3$. The decrease in loss by the addition of $MgTiO_3$ may be due to the separation of glassy phase of $Cu_{0.5}Ti_{0.5}NbO_4$ by $MgTiO_3$. When the glassy phase are continuous, loss current will be high at higher frequency. Addition of $MgTiO_3$ breaks the continuity of glassy and decreasing the loss at higher frequency.

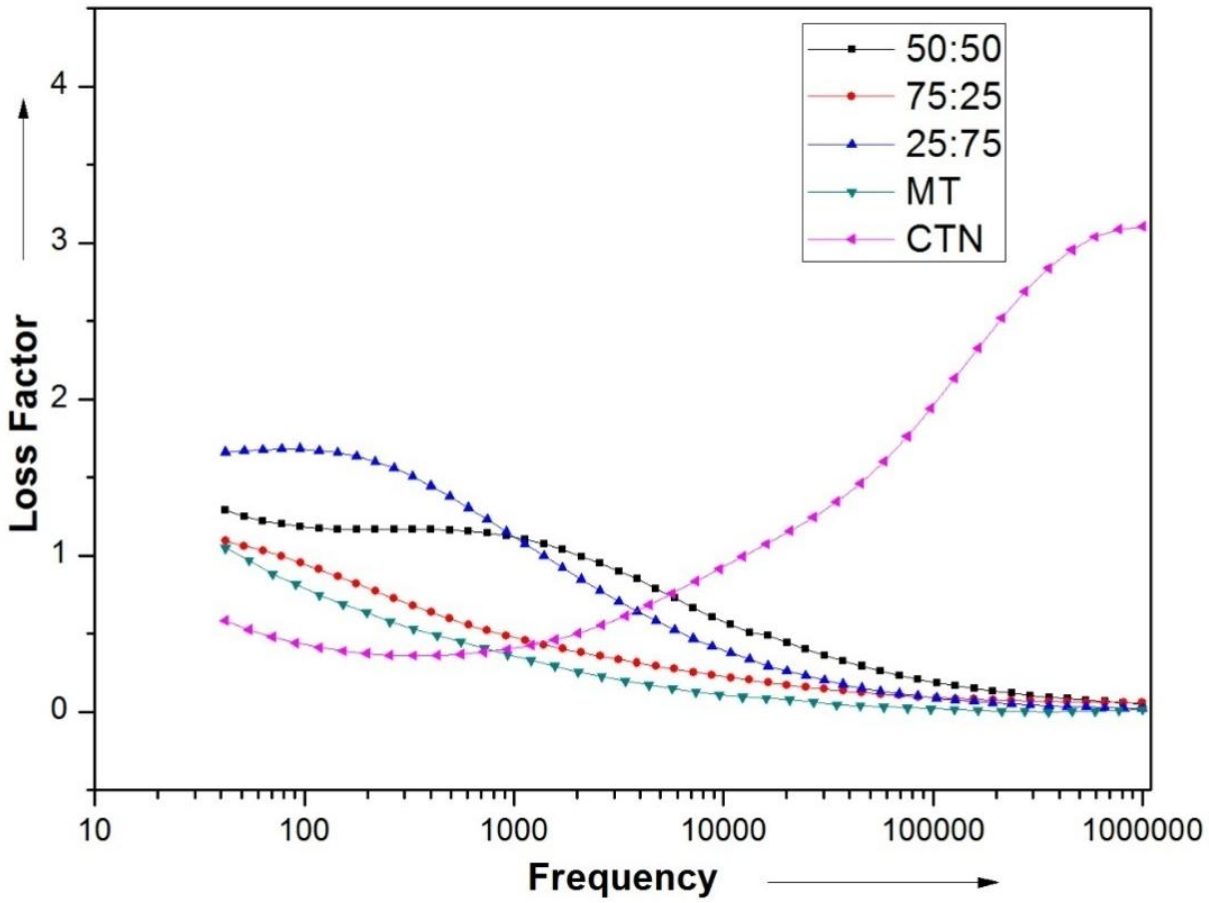

Fig. 13 V*variations of dielectric loss with frequency for different compositions.*

Impedance vs. Frequency

Fig. 14 shows the frequencies dependence of the impedance. It shows that the $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics has lowest impedance among all. This is due to the presence of conducting glassy phase in $Cu_{0.5}Ti_{0.5}NbO_4$ (CTN) ceramics. $MgTiO_3$ has the highest impedance as it is the most insulator among all. In general impedance of all the ceramics decreases with the increase in frequency.

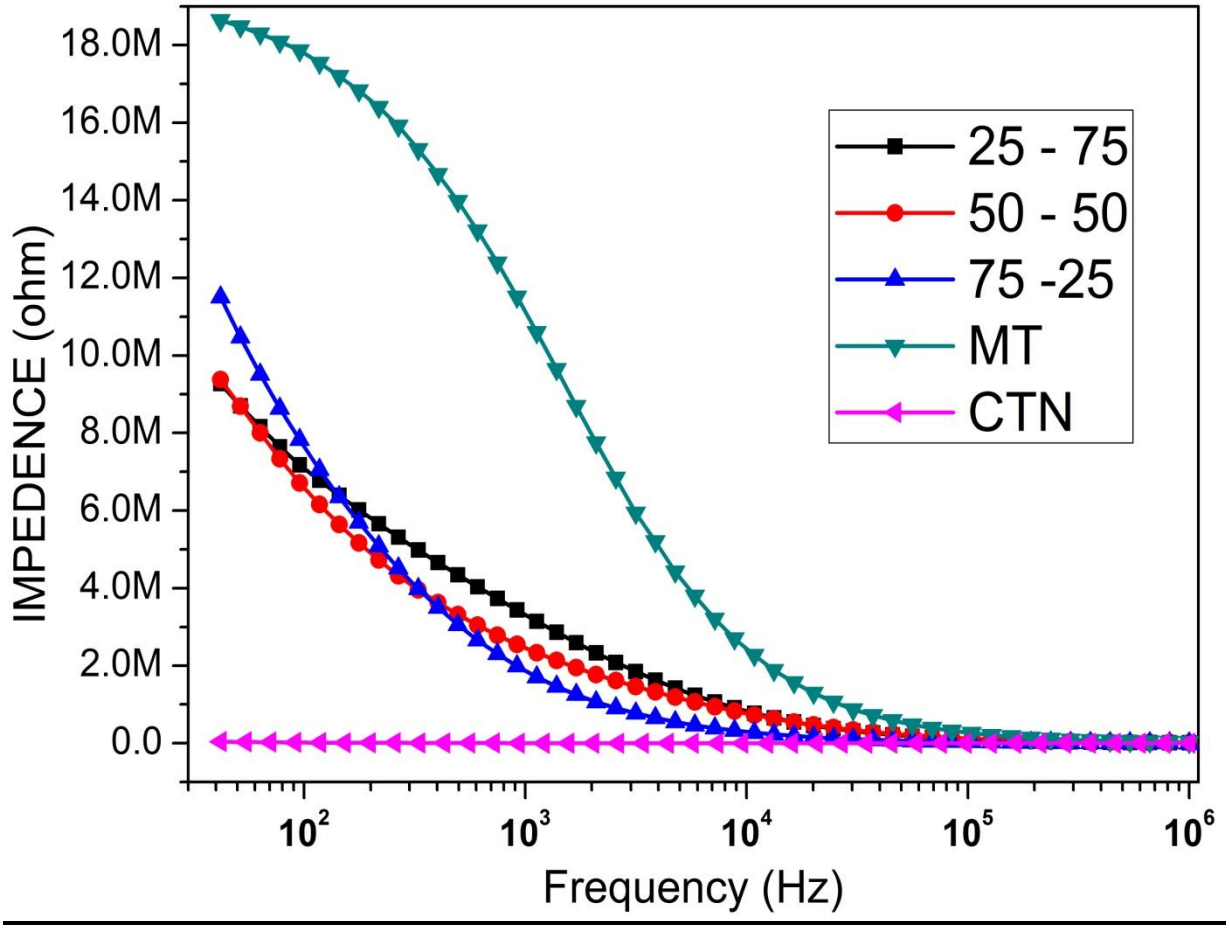

***Fig. 14 V**ariations of impedance with frequency for different compositions.*

Table 4 *Bulk density and Apparent Porosity for different compositions.*

Serial Number	**Composition**	**Bulk Density**	**Apparent Porosity**
O1.	$Cu_{0.5}Ti_{0.5}NbO_4$	4.75	3.37
02.	$MgTiO_3$	2.63	30.93
03.	50% $Cu_{0.5}Ti_{0.5}NbO_4$-50% $MgTiO_3$	3.71	5.16
04.	25% $Cu_{0.5}Ti_{0.5}NbO_4$-75% $MgTiO_3$	3.60	5.09
05.	75% $Cu_{0.5}Ti_{0.5}NbO_4$-25% $MgTiO_3$	4.13	3.62

Conclusion

$MgTiO_3$ and $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics where successfully synthesised through solid oxide reaction route. Pure $MgTiO_3$ phase powder was formed at a calcination temperature of 1000^oC. The two ceramics were mixed in a volume proportion of 25:75, 50:50 and 75:25. The sintering temperatures of these composites were found to decrease with the increase in $Cu_{0.5}Ti_{0.5}NbO_4$ content in the composites. The ceramics were sintered in the temperature range of 1065^oC-1190^oC. The bulk density of composites increased with the increase in $Cu_{0.5}Ti_{0.5}NbO_4$ content; due to the liquid phase formation by the addition of $Cu_{0.5}Ti_{0.5}NbO_4$. The apparent porosity was almost similar in all the ceramics. The microstructural investigation shows a porous microstructure and separation of copper based liquid phase.

Permittivity of $MgTiO_3$ was lowest and $Cu_{0.5}Ti_{0.5}NbO_4$ was highest at 1MHz frequency. Permittivities of composites were in between two end members. Dielectrics loss of $MgTiO_3$ was lowest and the loss decreases with the increase in frequency. However, dielectric loss of $Cu_{0.5}Ti_{0.5}NbO_4$ was very high which increases with the increase in frequency.

Similarly, impedance of $Cu_{0.5}Ti_{0.5}NbO_4$ was lowest and that of $MgTiO_3$ was highest. From the results it may be concluded that $MgTiO_3$ and $Cu_{0.5}Ti_{0.5}NbO_4$ composites ceramics are suitable for high frequency application and their properties can be tuned depending on composition.

References

[1] Joseph S, Suresh MK, Thomas JK, John A, Solomon International Journal of Applied Ceramic Technology 2010;7:E129-34.

[2] Zhang QL,Yang H,Zou JL.Materials Letters 2008;62:3872-4.

[3] Huang CL, Yang WR.Materials Letters 2009; 63:103-5.

[4]Axelsson AK, Pan Y, Valant M, Alford N, Journal of the American Ceramic Society 2009:92:1773-8.

[5]CFT Seng, Journal of European Ceramic Society 35(2015) 383-387.

[6] Ching-Fang Tseng, Chao-Chen Chen, Chen-Wei Lin, Materials Chemistry and Physics 147 (2014) 535-539.